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**Influence of the Sulfonate Counteraction on the Thermal Stability
of Nafion® Perfluorosulfonate Membranes**

by

D. L. Feldheim, D. R. Lawson and C. R. Martin

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**Influence of the Sulfonate Counteraction on the
Thermal Stability of Nafion® Perfluorosulfonate Membranes**

by



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Abstract

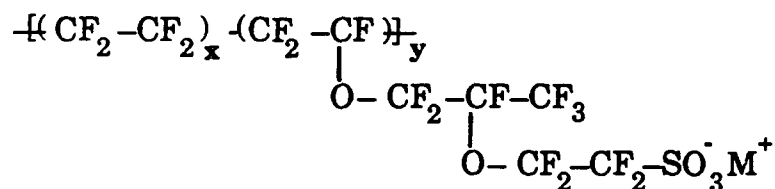
We report in this paper a strong dependence of the thermal stability of Nafion perfluorosulfonate ionomer on the nature of the counterion associated with the fixed sulfonate site. These results were obtained using thermal gravimetric analysis on a series of alkali metal and alkyl ammonium cation-exchanged Nafion films. We have found that the temperature of decomposition of Nafion is inversely dependent on the size of the exchanged cation; i.e. Nafion films show improved thermal stability as the size of the counter cation decreases. We attribute this inverse relationship of thermal stability with counterion size to an initial decomposition reaction which is strongly influenced by the strength of the sulfonate-counterion interaction.

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Introduction

Perfluorosulfonate ionomers (PFSI's) are a class of ion-exchange polymer with excellent chemical, mechanical and thermal stability (1-3). As a result, these polymers can be used in aggressive chemical environments such as highly caustic solutions at elevated temperatures (4). PFSI's have been used as separator membranes in chlor-alkali cells (4), water electrolyzers (5), batteries (6,7) and fuel cells (8-10). The most well known of these polymers is du Pont's Nafion; the structure for the commercially-available 1100 equivalent weight version of Nafion is shown below (11).



$$x = 6.6$$

Nafion contains a polytetrafluoroethylene (PTFE) backbone with an ether-linked sidechain terminating in a sulfonate cation exchange site; M^+ represents the countercation associated with this fixed SO_3^- site. For the commercially available material $X=6.6$, meaning that there are 6.6 tetrafluoroethylene units for every one fluoroether sidechain.

Nafion has been characterized using a wide variety of physical methods (1-3, 12, 13). However, the influence of the ion-exchange site on the thermal stability of the polymer has not yet been fully elucidated. For example, previous studies have characterized the thermal stability of only the proton and potassium-forms of the polymer (14-16). There has been no systematic investigation of the influence of the countercation on the thermal stability of Nafion. In this paper, we present the results of a systematic investigation of the effect of the countercation on the thermal stability of Nafion membranes.

Experimental

Thermal analyses were carried out using a du Pont 9900 Thermal Analysis System. This system contains data-analysis software that determines decomposition onset temperatures via extrapolation. This program was used for all decomposition temperatures reported herein. Thermal gravimetric analyses were carried out at scan rates of 10°C/minute under nitrogen. Elemental analyses were carried out by Galbraith Laboratory in Knoxville, TN. Before use, the Nafion membranes (du Pont, 1100 equivalent weight) were cleaned extensively using a procedure described previously (10). The H⁺-form films, prepared in this manner, were stored in purified water (Millipore) before ion-exchange.

Alkali metal cations were incorporated into the Nafion films using solutions of the cation-chloride salt. Typically, a one cm² piece of Nafion film was placed in ca. 250 mL of a 2M aqueous solution of the appropriate salt. The film was allowed to equilibrate in the stirred solution for approximately 48 hours. This exposure is sufficient to completely replace H⁺ with the desired cation (17). Following exchange, the films were stirred in purified water to remove excess salt from the film. The metal cation-exchanged films were dried in a vacuum oven for approximately 24 hours at 100°C prior to thermal characterization.

In addition to the alkali metal-form Nafion films, the following alkyl ammonium cations were investigated: tetramethyl (TMA), tetraethyl (TEA), tetrabutyl (TBA), tetraheptyl (THA), and decyl-tridodecyl (DTD). Solutions of the bromide and iodide alkyl ammonium salts were used to exchange these cations into the polymer. Due to the limited solubility of the larger alkyl ammonium cations in water, the entire series of alkyl ammonium salts was dissolved and exchanged into Nafion using ethanol as solvent. Three to four days of equilibration were used to ensure complete exchange of the quaternary counterions. Martin and Freiser have shown Nafion shows tremendous preference for the alkylammonium ions, relative to H⁺ (18). Following exchange, the films were exposed to neat ethanol in order to remove excess quaternary salts from the PFSI membrane. The quaternary ammonium-exchanged films, obtained in this manner, were dried in vacuum for approximately 24 hours at 50°C.

Results

Representative TGA scans for three alkali metal-exchanged Nafion films are shown in Figure 1. These films show essentially no mass loss up to ca. 400°C. Above this temperature, however, appreciable mass loss is seen. Note that the onset temperature of thermal decomposition is dependent on the exchanged alkali metal counterion (Figure 1). Above the onset temperature, the TGA scans show several steps that we attribute to sequential breakdown of the various regions of the polymer (see below). Figure 2 presents representative TGA scans for three alkyl ammonium-exchanged Nafion films. These films show little or no mass loss below 300°C. Above this temperature, as with the alkali metal-exchanged films, we see onset of mass loss that is dependent on the nature of the alkyl ammonium counterion. Above the onset of thermal decomposition, these films also display distinct mass loss regions, which are discussed in greater detail below.

The onset decomposition temperatures, determined from the TGA scans for the five alkali metal-exchanged Nafion films studied, are presented in Table 1. The thermal stabilities of the alkali metal-exchanged Nafion films follow the trend shown below.



The analogous data for the alkyl ammonium-exchanged Nafion films are also presented in Table 1. The thermal stabilities of these alkyl ammonium films follow the trend shown below.



Within each of the series of cations studied, the thermal stabilities of the Nafion membranes increases linearly as the diameter of the incorporated cation decreases with the exception of the Li⁺-form films in the alkali metal series and DTD in the alkyl ammonium-form films (Figures 3 and 4). We attribute the anomalous decomposition temperature of Li⁺-form films to the large hydration energy of Li⁺. This hydration energy leads to a greater extent

of water association, which results in a larger effective diameter and lower charge density for lithium. It is not unexpected that lithium films retain water even at the elevated temperatures of the present study (19). Eisenberg and Yeo have attributed a similar anomaly in the cluster glass transition for lithium-form films to residual waters of hydration (20). With respect to the trends for the alkyl ammonium films, THA and DTD films have a similar decomposition temperature. From the trends observed with smaller cations, we would expect DTD films to have a significantly lower decomposition temperature than THA due to its larger size. The similarity in decomposition may result from an upper limit on size effects on the interaction strength.

Discussion

The simplest starting point from which to rationalize the cation-induced changes in thermal stability for Nafion would seem to be the thermal decomposition behavior of the simple inorganic metal sulfonates (21). However, the decomposition temperatures for the metal sulfonates increase as the size of the alkali metal cation of the salt increases. The opposite trend is observed for Nafion (Table 1). The decomposition products in the case of the metal sulfonates is the metal oxide and SO_2 (22). We have conducted elemental analyses for sulfur on Cs^+ -form Nafion films before and after raising the temperature of the film above the decomposition temperature. The initial sulfur content was 3.2%; after the high temperature treatment, the sulfur content was 3.0%. Analogous results were obtained for K^+ -form films (16). Hence, formation of SO_2 is not the decomposition mechanism for the Nafion-alkali metal ion films. Since the decomposition products for the metal sulfonates and for the metal ion-substituted Nafion films are clearly different, it is not surprising that the trends in their decomposition temperatures with respect to cation size are different.

Clues to the mechanism of the thermal decomposition process in Nafion are obtained from the shape of the TGA profiles. The TGA scans presented in Figures 1 and 2 show step-like mass losses as the temperature is scanned past the onset of decomposition. We attribute these breaks in the mass-loss slope to the sequential decomposition of the Nafion membrane. In the case of the alkali-metal films, two steps are readily apparent in the TGA scans (Figure 1). The initial step appears at ca. 30% mass loss. For Na^+ , K^+ , and Cs^+ films the

side chain makes up 29.3, 28.9 and 26.7% of the mass of the film respectively (excluding sulfur which is not lost upon decomposition, see above). We conclude, therefore, that the side chain decomposes initially (14-16), followed by the PTFE backbone.

The decomposition of the alkyl ammonium-exchanged films also appears to begin with the ether-linked side chain. For TMA, TEA, and DTD films the sidechain makes up 30.8, 29.4, and 20.7% of the mass of the films, respectively. These percentages are in qualitative agreement with the mass loss observed in the initial step of the TGA scans shown in Figure 2 (26, 24 and 15% for the TMA, TEA, and DTD films, respectively). A complicating factor in the subsequent decomposition reactions is the possible decomposition of the tetraalkyl ammonium cation, itself. Although not apparent in the smaller alkyl ammonium cation-exchanged films, a second step is apparent in the TGA scans of THA and DTD ammonium-exchanged films. The mass loss associated with this second step is in qualitative agreement with the relative mass of the counterion. The remainder of the mass loss is assigned to the decomposition of the Nafion PTFE backbone.

Conclusions

The stability of various alkali metal and alkyl ammonium substituted films was investigated using thermal gravimetric analysis. We have found that the stability of the Nafion film is directly related to the size of the counterion. In addition, there is evidence for a stepwise decomposition mechanism.

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**Table 1. Values of onset decomposition temperature for alkali metal
and alkyl ammonium exchanged Nafion membranes.**

Cation	Decomposition Temperature
Li+	426°C
Na+	458°C
K+	445°C
Rb+	430°C
Cs+	426°C
+NMet ₄	416°C
+NEt ₄	390°C
+NBu ₄	339°C
+NHep ₄	304°C
+NDecyl-Dodecyl ₃	302°C

Figure Captions

- Figure 1. Thermal gravimetric scans of Na^+ (—), K^+ (— —), and Cs^+ (- - -) exchanged Nafion films. Scan rate $10^\circ\text{C}/\text{min}$ under nitrogen.
- Figure 2. Thermal gravimetric scans of TMA (—), TBA (— —), and THA(- - -) exchanged Nafion films. Scan rate $10^\circ\text{C}/\text{min}$ under nitrogen.
- Figure 3. Onset of thermal decomposition versus ionic radius for the alkali metal-form Nafion films. Dots are the unhydrated cations (mean ionic radii)(23). The X is the hydrated radius of lithium at ambient temperature (24). Note that at these temperatures the radius of Li^+ probably lies between the mean value (the dot) and the hydrated value (X).
- Figure 4. Onset of thermal decomposition versus number of carbons in the alkylammonium cation (i.e. four for TBA+) for substituted Nafion films.

TGA

